

Determination of Molar Gibbs Energies and Entropies of Mixing of Melts in Binary Subsystems of the System $\text{CaO} \cdot \text{SiO}_2$ — $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ — $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$

II. The System $\text{CaO} \cdot \text{SiO}_2$ — $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$

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Composition and temperature dependences of component activities in the melt system $\text{CaO} \cdot \text{SiO}_2$ — $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ were determined by means of the phase diagram as well as primary composition and temperature dependence of relative enthalpy of melts. Using the activities, composition and temperature dependences of Gibbs energy and entropy of mixing were calculated. On the basis of the course of these dependences it can be concluded that the melts of this subsystem behave like general solutions.

The procedure for calculation of component activities in binary melt systems was theoretically derived in the previous paper [1]. The enthalpies of mixing for these systems are indirectly determined by means of composition and temperature dependence of the relative enthalpy. In such case it is necessary to consider especially the errors of the enthalpy of mixing that are much more higher than if it is determined directly. This procedure was in [1] applied to the $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (C_2AS)— $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (CAS_2) system. The calculation of activities in this system was simple because of zero values of enthalpy of mixing at all compositions and entire temperature range studied.

The subject of this work is to determine molar quantities of mixing for the melts in the $\text{CaO} \cdot \text{SiO}_2$ (CS)— $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (CAS_2) system. The enthalpy of mixing in these melts is already dependent both on composition and temperature.

THERMODYNAMIC ANALYSIS OF MELTS IN THE CS — CAS_2 SYSTEM

We will use symbols X for CS and Y for CAS_2 in the following text. Chosen quantities will be denoted by subscript c and the ones corresponding to multiphase equilibria by subscript eq. All systems under study will be in equilibrium state.

Thermodynamic analysis of this system is based on two things available:

a) primary dependence of relative enthalpy of the melts in the CS — C_2AS — CAS_2 system [1],

b) phase diagram for the CS — CAS_2 system constructed by data optimization [2, 3] (Fig. 1). All measurements of this phase diagram from 1942

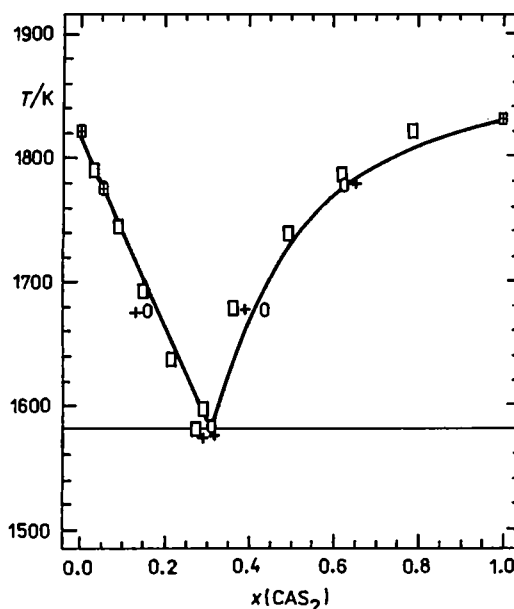


Fig. 1. Phase diagram of the CS — CAS_2 system according to literature. \square [2], $+$ [3], \circ [4].

to 1963 were taken into account including also information about the ways of measuring. During optimization the phase diagram was correlated with the one of the ternary system CaO — Al_2O_3 — SiO_2 [4]. As for the reliability of the phase diagram, it is discussed in [5].

Into the Le Chatelier—Shreder equation (1) in [1] (activity of the component in the crystalline state $a_{X(Y),\text{cryst}} = 1$) the relation

$$\Delta H_{\text{fus},X(Y)}(T) = H_{\text{rel},X(Y),\text{melt}}^{\circ}(T) - H_{\text{rel},X(Y),\text{cryst}}^{\circ}(T) \quad (1)$$

was substituted. $H_{\text{rel},X(Y),\text{melt}}^{\circ}(T)$ and $H_{\text{rel},X(Y),\text{cryst}}^{\circ}(T)$ are the relative enthalpies for melt and crystalline component X(Y), respectively. The values of $H_{\text{rel},X(Y),\text{melt}}^{\circ}(T)$

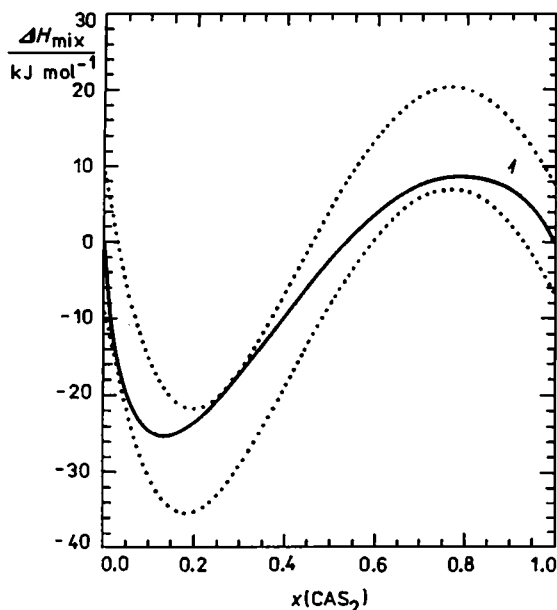


Fig. 2. Substitute function $\Delta H_{\text{mix}}(x(\text{CAS}_2)) (T)$ at the temperature 1600 K and error interval ($\pm 3\sigma$) related to $\Delta H_{\text{mix}}(x(\text{CAS}_2))$ calculated using primary dependence $H_{\text{rel}}(x_Y, T)$.

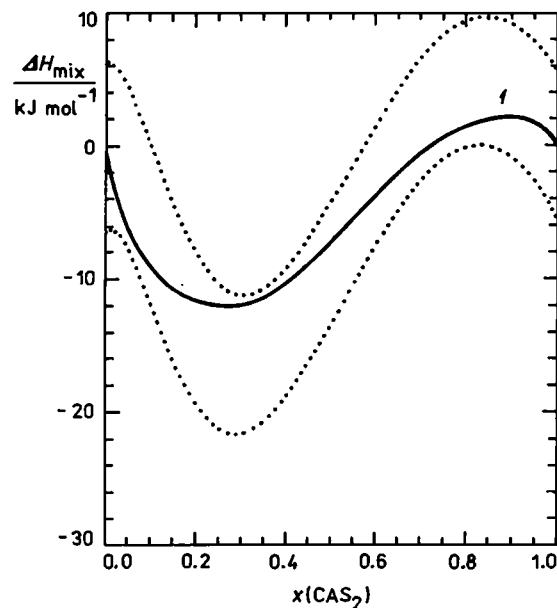


Fig. 3. Substitute function $\Delta H_{\text{mix}}(x(\text{CAS}_2)) (T)$ at the temperature 1950 K and error interval ($\pm 3\sigma$) related to $\Delta H_{\text{mix}}(x(\text{CAS}_2))$ calculated using primary dependence $H_{\text{rel}}(x_Y, T)$.

were taken from [1], $H_{\text{rel}, X, \text{cryst}}^{\circ}(T)$ from [6, 7] and $H_{\text{rel}, Y, \text{cryst}}^{\circ}(T)$ from [8, 9]. Composition dependence $\ln a_{\text{eq}, X(Y)}(x_Y)$ was determined from the values of $\ln a_{\text{eq}, X(Y)}(T_{\text{eq}, X(Y)}(x_{Y, c}))$ calculated from (1) in Ref. [1].

Activities for both components at the temperature T_c were calculated from eqns (2) and (3) in Ref. [1]. The values of $\Delta \bar{H}_{\text{mix}, X}(x_Y, T_c)$ calculated from the dependence $\Delta H_{\text{mix}}(x_Y, T_c)$ were at the compositions close to the pure CS so low that the regression function $a_X(x_Y, T_c)$ was not monotonous and therefore unreal for melt in equilibrium. Therefore we had to use, like in [1], instead of $\Delta H_{\text{mix}}(x_Y, T_c)$ the substitute dependence. For compositions $x_Y \in \langle 0, x_{Y, \text{out}} \rangle$ the developing function l from eqn (5) [1] was used. By the iterative method such value for constant $\kappa(T_c)$ was found that the deviation of substitute function $\Delta H_{\text{mix}}(x_Y, T_c)$ from the original one at the temperatures 1600 K to 1950 K and mentioned compositions might be less than 3σ . Such determined value of $\kappa(T_c)$ lies within the interval $\langle 0.0011 \text{ K}^{-1}, 0.0034 \text{ K}^{-1} \rangle$. At compositions

$x_Y \in \langle x_{Y, \text{out}}, 1 \rangle$ the substitute function was expressed according to [1] by a third-order polynomial which also describes $\Delta H_{\text{mix}}(x_Y, T_c)$ with an error less than 3σ . The courses of substitute function $\Delta H_{\text{mix}}(x_Y)$ at temperatures 1600 K and 1950 K including the error limits related to $\Delta H_{\text{mix}}(x_Y)$, calculated using primary dependence of $H_{\text{rel}}(x_Y, T)$, are shown in Figs. 2 and 3, respectively.

Dependence of $\ln a_{X(Y)}(x_Y, T_c)$ was described similarly as in [1] by the Margules equation (15). To determine coefficients in (15) the conditional relations

$$a_{X(Y)}(x_{X(Y)} = 1, T_c) = 1 \quad (2)$$

$$\frac{d \ln a_{X(Y)}(x_{X(Y)} = 1, T_c)}{dx_Y} = \frac{d \ln a_{\text{eq}, X(Y)}(x_{X(Y)} = 1, T_{\text{fus}, X(Y)})}{dx_Y} \quad (3)$$

and nine values of activities (three of them for compositions $x_Y \in \langle 0, x_{Y, \text{out}} \rangle$ and six for compositions $x_Y \in \langle x_{Y, \text{out}}, 1 \rangle$) calculated from eqns (2) and (3) in [1] at the temperatures 1600 K to 1950 K by 50 K were used (Table 1). Comparing the

Table 1. Starting Values of CS and CAS_2 Activities Used for the Margules Equation Coefficients Calculation

$x(\text{CAS}_2)$	a	T/K							
		1600	1650	1700	1750	1800	1850	1900	1950
0.1	(CS)	0.764	0.797	0.824	0.848	0.866	0.881	0.891	0.899
0.2		0.641	0.686	0.726	0.760	0.789	0.812	0.831	0.845
0.3		0.580	0.631	0.676	0.716	0.751	0.781	0.805	0.825
0.4	(CAS ₂)	0.515	0.476	0.447	0.426	0.410	0.399	0.391	0.387
0.5		0.746	0.694	0.652	0.617	0.590	0.568	0.553	0.542
0.6		0.901	0.852	0.809	0.773	0.743	0.718	0.699	0.686
0.7		0.942	0.910	0.882	0.856	0.834	0.815	0.800	0.789
0.8		0.949	0.931	0.917	0.905	0.895	0.887	0.880	0.875
0.9		0.981	0.973	0.967	0.961	0.956	0.951	0.947	0.943

number of conditions ($2 \times 2 + r + 1 + n$) [1] and coefficients ($2 \times (2 + r)$) in (15) [1] we get r equal to 10. There are two temperature independent and ten temperature dependent coefficients in the Margules equation. Temperature dependences of the coefficients were expressed by the relation

$$K_{X(Y),i}(T) = \sum_{j=1}^5 K_{X(Y),i,j} T^{j-1} \quad (4)$$

Plots of $a_{X(Y)}(x_Y, T_c)$ at the temperatures 1600 K and 1950 K are shown in Fig. 4.

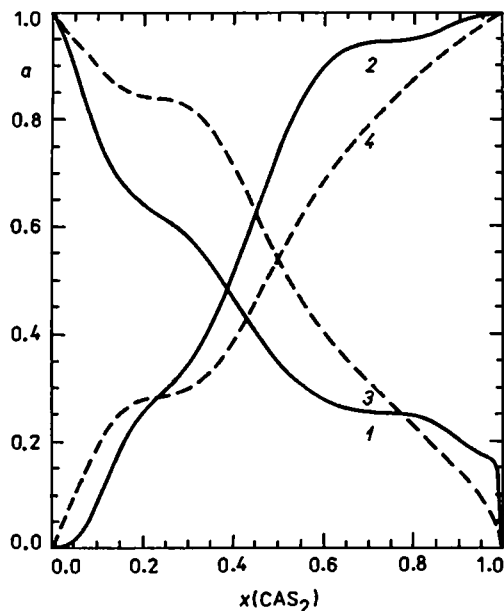


Fig. 4. Composition dependence of activities for CS (1 and 3) and CAS_2 (2 and 4) at the temperature 1600 K and 1950 K, respectively.

If we substitute into eqn (17) in [1] relations (15), for both components we get for the melts of the CS— CAS_2 system composition and temperature dependence of Gibbs energy of mixing. From eqn (18) in [1] we obtain the same dependence for entropy of mixing.

Dependences $\Delta G_{\text{mix}}(x_Y, T_c)$, $\{\Delta H_{\text{mix}}(x_Y, T_c) = \Delta G_{\text{mix}}(x_Y, T_c) + T\Delta S_{\text{mix}}(x_Y, T_c)\}$, and $-T\Delta S_{\text{mix}}(x_Y, T_c)$ are at the temperatures 1600 K and 1950 K shown in Figs. 5 and 6.

As follows from these figures, the melts of the CS— CAS_2 system behave in the temperature range under study as general solutions. Nonzero values of enthalpies of mixing are consequence of reactions between particles of both components and therefore of their structural difference.

REFERENCES

1. Proks, I., Strečko, J., Kosa, L., Nerád, I., and Adamkovičová, K., *Chem. Papers* 47, 3 (1993).
2. Osborn, E. F., *Am. J. Sci.* 240, 751 (1942).

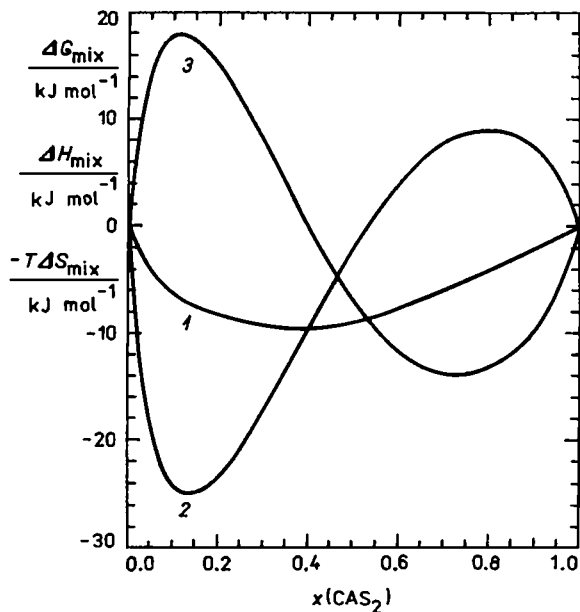


Fig. 5. Isothermal dependences of the quantities $\Delta G_{\text{mix}}(x_Y)$ (1), $\Delta H_{\text{mix}}(x_Y)$ (2), and $-T\Delta S_{\text{mix}}(x_Y)$ (3) of the system CS— CAS_2 at the temperature 1600 K.

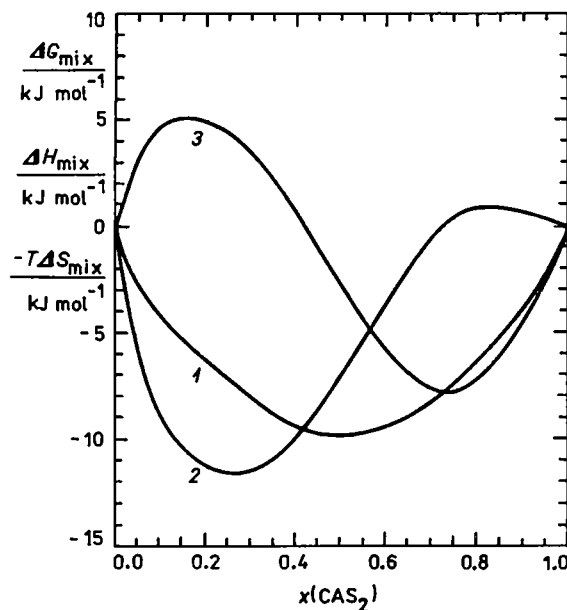


Fig. 6. Isothermal dependences of the quantities $\Delta G_{\text{mix}}(x_Y)$ (1), $\Delta H_{\text{mix}}(x_Y)$ (2), and $-T\Delta S_{\text{mix}}(x_Y)$ (3) of the system CS— CAS_2 at the temperature 1950 K.

3. Gentile, A. L. and Foster, W. R., *J. Am. Ceram. Soc.* 46, 76 (1963).
4. Osborn, E. F. and Muan, A., *Phase Equilibrium Diagrams of Oxide Systems. Plate 1, The System CaO— Al_2O_3 — SiO_2* . The American Ceramic Society, Columbus, Ohio, 1960.
5. Eliášová, M., Žigo, O., and Proks, I., *Chem. Papers*, in press.
6. Adamkovičová, K., Kosa, L., and Proks, I., *Silikáty* 24, 193 (1980).
7. Adamkovičová, K., Kosa, L., Proks, I., and Žigo, O., *Chem. Papers* 42, 731 (1988).
8. Richet, P. and Fiquet, G., *J. Geophys. Res.* 96, 445 (1991).
9. Kosa, L., Žigo, O., Adamkovičová, K., and Proks, I., *Chem. Papers* 41, 289 (1987).

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